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Development and Use of Baking Powder and Baking Chemicals

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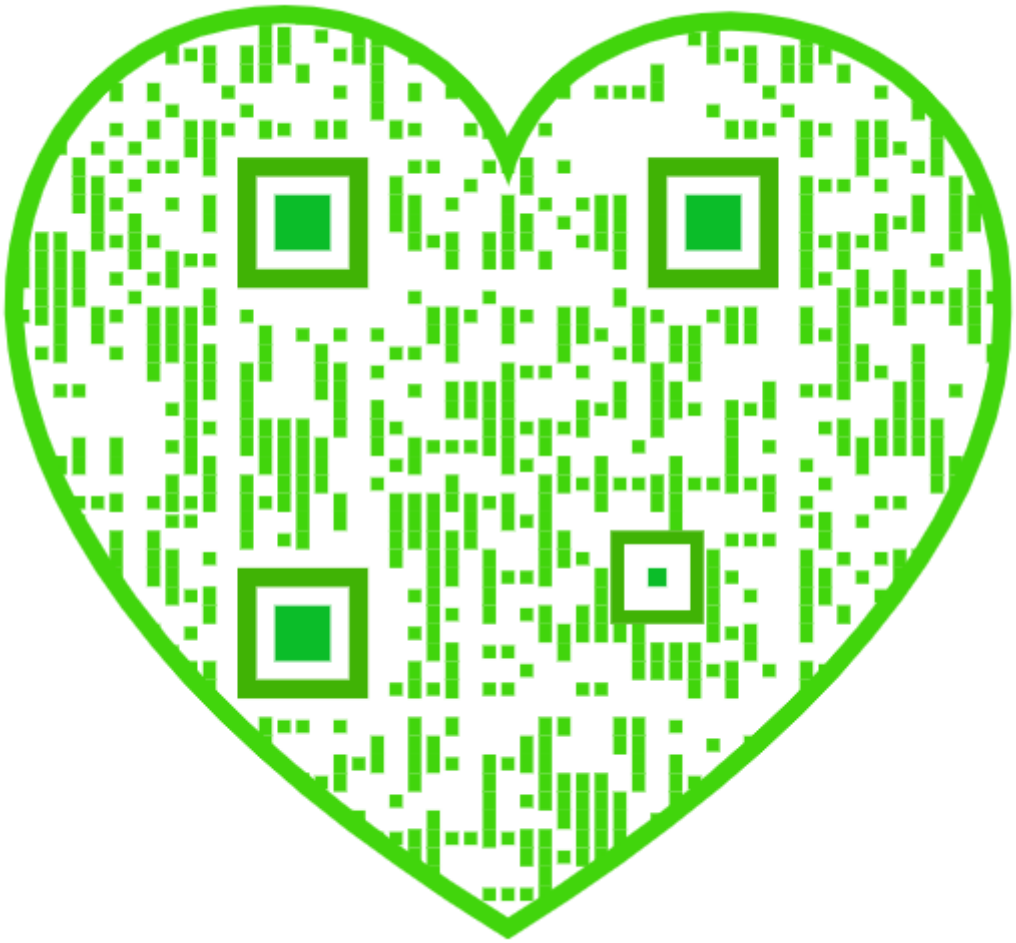
INTRODUCTION

Baked products become light, as a rule, by the expansion of the carbon dioxide which is evolved within the dough or batter during its preparation and in the early stages of baking. The carbon dioxide may be produced by yeast, baking powder, or baking chemicals. Yeast is used in making bread, rolls, and certain types of biscuits and crackers, whereas baking powder and baking chemicals are used in most other baked products. Considerable time is required for the production of the carbon dioxide by yeast, but with baking powder a part of the gas is liberated as soon as the liquid is added and the remainder when heat is applied as in baking.

HISTORY OF LEAVENING

Leavening was practiced by the Eygptians, and the practice was handed down by them to the Greeks and by the Greeks to the Romans (*14, v. 1, p. 664*).[1]

[1] Italic numbers in parentheses refer to Literature Cited, p. 16.



From the time of the Romans to the present, the use of leavening has been common. In the early days leavening was ordinarily accomplished by growing yeast or yeasts in a dough or batter rich in carbohydrates. The enzymes of the yeast act upon the carbohydrates, forming carbon dioxide and alcohol. The carbon dioxide gas permeates the dough and intermingles with it; when heat is applied, as in baking, the gas expands, and produces a porous mass. As the heat continues the framework becomes more solid, and an open spongelike product results.

One of the early types of leavened bread was known as salt-rising bread. The gas which leavens bread of this type is furnished by bacteria, such as *Bacillus welchii*, instead of yeast. Formerly it was made by allowing a mixture of wheat meal, corn meal, salt, and hot milk to stand in a warm place for several hours, when gas was produced and the mass became porous. Flour was added to make a dough, and it was then allowed to rise and was baked in the usual manner.

Such spontaneous fermentation lacked uniformity, however, and the results were very uncertain. Today practically all salt-rising bread is made with a commercial "salt rising" yeast, which is a culture of the bacteria that furnish the gas for leavening. With this culture the results are much more uniform and dependable.

Three-quarters of a century ago there was brought out in England a method of making aerated bread without the use of either yeast or baking powder. This method consisted in mixing flour with water that was charged with carbon dioxide, the mixing being done under pressure which ranged from 40 to 200 pounds. After it was mixed, the dough was released into pans. With the removal of the pressure and with the heat of the oven the carbon dioxide expanded and produced a leavened loaf. Aerated bread also was made to a very limited extent in France, Germany, and the United States.

Yeast requires considerable time to produce sufficient carbon dioxide to properly leaven a product. To obviate this delay, it became customary for the housewife to use sour milk and soda to supply the carbon dioxide necessary to leaven certain of her baked products. Because all sour milk does not possess the same degree of acidity, there has always been uncertainty as to how much soda should be used to neutralize the acid. If too much soda is used, undesirable products result.

Chemical leavening by means of a carbonated alkali and muriatic acid was proposed as early as the latter part of the eighteenth century and has occasionally been suggested in the literature until as recently as 1916, but this means of leavening has never been generally employed.

Baking powder was the natural sequel to the early methods of leavening. The first formulas for baking powder were developed in the United States in 1850. In that year a cream of tartar baking powder was sold by Preston & Merrill of Boston.

In 1853 Vincent C. Price, of Troy, N. Y., is said to have compounded a baking powder consisting of cream of tartar and soda, with starch or flour as a stabilizing ingredient. The first reference to baking powder in scientific literature appeared in the Archiv der Pharmacie in 1855 (*11*). The author, E. Reichardt, investigated an

American baking powder containing cream of tartar as its acid ingredient.

In 1865 Dr. Price, then at Waukegan, Ill., established a small trade in "Dr. Price's Cream Baking Powder." In 1868 another cream of tartar baking powder was launched in Fort Wayne, Ind., by Hoaglands, a firm of druggists.

In 1856 Eben Norton Horsford, a professor in Harvard University, took out a patent for the preparation of monocalcium phosphate (*8*). This process consisted in mixing partly charred bones with sulfuric acid and leaching. The resultant phosphoric acid was concentrated in iron kettles over a coke fire and a calculated quantity of bone ash was added from time to time until the mixture became pasty. After cooling it was mixed with starchy material, forming an acid product which had a neutralizing value such that 2 parts of the mixture were required to neutralize 1 part of soda. The acid mixture required several weeks to dry and cure. It was spread out in thin layers on the floor and broken up and turned over from time to time.

Following the issuance of the patent there appeared on the market Horsford's Bread Preparation, which was put up in two paper packages wrapped together, one containing monocalcium phosphate and the other bicarbonate of soda. In the early days a wooden measuring device accompanied the packages, the cavity on one side of the block being double the capacity of the cavity on the other side. The housewife was directed to fill the larger cavity with the acid phosphate and the smaller one with bicarbonate of soda and add both ingredients to a biscuit or cake dough. These packages may still be obtained.

The next step was the use of a can with two sections fitting into each other, one of which contained the phosphate and the other the soda. Later the ingredients were sold mixed together, but as the finely ground monocalcium phosphate as made at that time, when mixed with bicarbonate of soda and cornstarch, did not keep well in commercial tin cans it was marketed in glass bottles and sold under the name of "Yeast Powder." The first of these appeared in 1858, and they have continued to be sold in that form up to the present. Doubtless the bottles offer better protection against atmospheric moisture than did the cans.

Improvements in the process of manufacture and preparation of the ingredients were made from time to time, but it was not until 1893 that a complete phosphate baking powder was put up in tin cans and marketed commercially.

In 1864 Dr. Horsford obtained another patent (*9*) in which he described a mixed or double phosphate of calcium and sodium. Further patents on the manufacture of phosphates were granted in 1868. The process of manufacture then remained stationary for about 20 years. In 1888 experiments were made to produce a monocalcium phosphate of 80-percent neutralizing strength without the use of starchy material. In 1889 the first commercial material of that character was produced by mixing together a paste which contained monocalcium phosphate crystals suspended in concentrated phosphoric acid with the calculated quantity of bone ash. This was a distinct step forward in the manufacture of monocalcium phosphate, as up to that time it had been made with a neutralizing strength of only 45 to 50 percent. Some years later lime or limestone or

ground marble was substituted for the bone ash, producing material of similar characteristics.

More recently further improvements have been made in the manufacture of monocalcium phosphate. Nearly all manufacturers now use phosphoric acid that has been volatilized from phosphate rock. This acid is practically free of impurities, notably fluorine, which sometimes remained in the acid that was produced by treating the phosphate rock with sulfuric acid. When volatilized phosphoric acid is treated with the calculated amount of purified calcium hydroxide or carbonate, a highly purified monocalcium phosphate results.

The speed with which the monocalcium phosphate reacts with bicarbonate of soda is influenced by the conditions under which the phosphate is made. A recent patent (*13*) describes a process of producing anhydrous monocalcium phosphate. It is claimed that this product reacts slowly in the cold, so that most of the gas is liberated after heat is applied during the baking process.

In the early part of the nineteenth century alum and the potashes, which included pearlash and bicarbonate of potash, were used in the preparation of gingerbread (*16, p. 181*). After the successful introduction of cream of tartar baking powder other manufacturers, in an attempt to find a substitute that would be less expensive than cream of tartar, used burnt alum as the acid-reacting material in baking powder. The first official notice of alum baking powder appeared in the annual report of the United States Commissioner of Agriculture for the year 1878 (*5, p. 135*). The report of the chemist states that a sample of baking powder had been submitted for analysis, the composition of which was as follows: 3 parts starch, 1 part bicarbonate of soda, and 1 part alum.

That alum was frequently used in baking powders at this time is apparent from the comment of the Government chemist: "The presence of alum in the so-called baking powders on the market is almost invariable." The alum referred to here was undoubtedly either burnt potash or ammonia alum. About 1892 the manufacture of anhydrous sodium aluminum sulfate, now frequently referred to as S. A. S., became established and soon replaced the potash or ammonia alum previously used in baking powder. Owing to the similarity in composition of sodium aluminum sulfate, potassium alum, and ammonium alum, the first named has at times been referred to as an alum. One State, Wisconsin, requires by law that any compound of aluminum used as a constituent of baking powder shall be called "alum" on the baking powder label. In other States the compound used is called sodium aluminum sulfate.

Baking powders containing only sodium aluminum sulfate as the acid ingredient have practically disappeared from the market. In their stead have appeared combination powders which contain sodium aluminum sulfate and calcium acid phosphate in varying proportions.

Still other types of baking powder have been proposed from time to time, and some of them have been marketed on a large scale. Monosodium phosphate was used as the acid ingredient of a baking powder for several years, but, largely on account of the instability of this powder, it was finally abandoned.

Patents have been issued for the use of a number of organic acids as the acid constituents of baking powder, or baking acids; among

these may be mentioned acetonedicarboxylic acid (*1*), adipic, lactic, malic, mucic, phthalic-anhydride, and succinic acid. None of these acidic factors has had large commercial acceptance in baking powder. Either their acid properties are too weak or the keeping quality of the baking powder made with them has not proved satisfactory. Acetonedicarboxylic acid was proposed as a leavening agent alone, i. e., uncombined with soda, as upon the application of heat it would break up into acetone and carbon dioxide. The acetone is said to be completely volatilized at baking temperatures, and no solid residue would remain with such a leavening agent. Although this product was proposed several years ago it has never come into general use. Calcium lactate is now used with phosphates in a powder for commercial bakers.

There has been much controversy regarding the relative merits of the different baking powders, the principal point of discussion being the residue of the baking powder that remains in the baked product. The residue from a tartrate baking powder is largely potassium sodium tartrate; from a phosphate powder it is calcium and sodium phosphates; and from a combination sodium aluminum sulfate calcium acid phosphate powder the residues are sodium sulfate, sodium phosphate, and calcium and aluminum compounds. The soluble residues are all saline, and they differ with the different types of baking powders. The quantity of saline residues in the baked products leavened by any of the ordinary types of baking powder is too small to be injurious when these products are consumed in the proportion found in the average diet.

Questions regarding the influence of aluminum compounds on the nutrition and health of man were referred to the referee board of consulting scientific experts. The conclusions of this board were published in United States Department of Agriculture Bulletin 103 (*12*). In general, the board concluded that a baking powder containing a compound of aluminum is no more harmful than any other baking powder.

BAKING POWDER

Production and Export

According to the data collected in the Biennial Census of Manufactures, 141,707,536 pounds of baking powder were produced in the United States in 1937. This was valued at $15,400,497.

The exports of baking powder from the United States in 1938 were 2,731,162 pounds.[2] Baking powder was principally exported to Sweden, Cuba, Mexico, Panama, Newfoundland, Labrador, Hong Kong, and the Philippine Islands.

There has been a large decrease in the quantity of baking powder exported during the last 10 years, although during the same period domestic production has only slightly decreased.

In recent years there has been a large increase in commercial baking with a corresponding decrease in home baking. This has resulted in increased production of the commercial type of baking powder and a decrease of the household type.

[2] Data furnished by the U. S. Department of Commerce.

Definition and Standard

According to the definition and standard adopted by the United States Department of Agriculture (*15, p. 20*)—

> Baking powder. The leavening agent produced by the mixing of an acid-reacting material and sodium bicarbonate, with or without starch or flour. It yields not less than 12 percent of available carbon dioxide.
>
> The acid-reacting materials in baking powder are: (1) Tartaric acid or its acid salts, (2) acid salts of phosphoric acid, (3) compounds of aluminum, or (4) any combination in substantial proportions of the foregoing.

Although the substances named in this definition and standard for baking powder are the ones ordinarily used in commercial baking powders, manufacturers are not prohibited from using other harmless substances that may be found suitable for the purpose. If any substance that is not included among those mentioned in the definition is used in a baking powder, this fact should be plainly stated upon the label so that the purchaser will be fully informed.

Purity

As with other food products, it is desirable to have baking powders as free from impurities as it is feasible to make them. The responsibility of removing any metallic or other impurities that may be found in the raw materials from which baking powders are made rests with the manufacturers.

Classification

In the United States, baking powders may be classified according to their acid-reacting components into three general classes: Tartrate powders, the acid constituent of which is potassium acid tartrate (cream of tarter) with or without the addition of tartaric acid; phosphate powders, the acid constituent of which is calcium acid phosphate or sodium acid pyrophosphate; combination powders, the acid constituents of which are sodium aluminum sulfate and calcium acid phosphate.

In addition to these three general classes there may be considered a miscellaneous class. This includes baking powders in which is used some other acid or combination of acid-reacting materials, for example, sodium aluminum sulfate, lactic acid, mucic acid, monosodium phosphate, and calcium lactate.

Bicarbonate of soda is the alkaline salt now found in all baking powders. Magnesium carbonate was formerly used to a very limited extent. Cornstarch is used as a stabilizing diluent and a standardizing agent.

Chemical Composition

The approximate chemical composition of baking powders may be indicated by the following theoretical formulas for their manufacture. The examples shown are calculated to give a theoretical total carbon dioxide strength of 14 percent for the household baking powders and 17 percent for the commercial powder. The formulas are also based on chemically pure substances, and no allowance is made for the presence of moisture or other compounds.

In these formulas it is assumed that 100 pounds of the acid-reacting materials will neutralize, respectively, the following weights of

bicarbonate of soda: Cream of tartar, 44 pounds; tartaric acid, 116 pounds; monocalcium phosphate, 80 pounds; sodium aluminum sulfate, 104 pounds; sodium acid pyrophosphate, 75 pounds.

These theoretical values are seldom used in the commercial manufacture of baking powders. The manufacturers of baking powder chemicals are in a position to furnish formulas that will give optimum baking results with their materials. Practical formulas should be obtained from the manufacturers.

CREAM OF TARTAR AND TARTARIC ACID BAKING POWDER

	Percent
Sodium bicarbonate	26. 73
Cornstarch	22. 40
Tartaric acid	5. 97
Potassium bitartrate (cream of tartar)	44. 90
Total	100. 00

In the presence of moisture, a reaction occurs between the components of the baking powder, and carbon dioxide is liberated; in addition there are certain byproducts of reaction which for the most part remain as residues in the baked products. In the baking powder cited the residues are potassium sodium tartrate and sodium tartrate. The probable reactions may be indicated by the following equations:

$$KHC_4H_4O_6+NaHCO_3=KNaC_4H_4O_6+CO_2+H_2O$$

and

$$H_2C_4H_4O_6+2NaHCO_3=Na_2C_4H_4O_6+2CO_2+2H_2O.$$

CALCIUM ACID PHOSPHATE BAKING POWDER

	Percent
Sodium bicarbonate	26. 73
Cornstarch	39. 84
Calcium acid phosphate	33. 43
Total	100. 00

With phosphate baking powders the reactions are somewhat complicated, varying under different conditions. Three equations follow which represent reactions that may take place under favorable conditions. The third equation represents what probably takes place under conditions of baking.

$$2CaH_4(PO_4)_2+4NaHCO_3=2CaHPO_4+2Na_2HPO_4+4CO_2+4H_2O \quad (1)$$
$$3CaH_4(PO_4)_2+4NaHCO_3=Ca_3(PO_4)_2+4NaH_2PO_4+4CO_2+4H_2O \quad (2)$$
$$3CaH_4(PO_4)_2+8NaHCO_3=Ca_3(PO_4)_2+4Na_2HPO_4+8CO_2+8H_2O \quad (3)$$

The first equation indicates a residue of dicalcium phosphate and disodium phosphate. The other two indicate the formation of tricalcium phosphate and monosodium or disodium phosphate.

COMBINATION BAKING POWDER (S. A. S. PHOSPHATE)

	Percent		*Percent*
Sodium bicarbonate	26. 73		26. 73
Cornstarch	40. 07		42. 97
Monocalcium phosphate	13. 28	or	4. 62
Sodium aluminum sulfate (calcined)	19. 92		25. 68
Total	100. 00		100. 00

With a combination baking powder the reactions are more complicated than with a straight phosphate powder. Besides the reaction of the phosphate and S. A. S. with the soda, there is probably an interreaction between the two.

The three types of baking powder mentioned above are estimated to constitute more than 90 percent of the baking powder produced in the United States. The combination powders represent a large proportion of the total production.

One type of leavening seems to be gaining favor with commercial bakers. In this the gas is produced by the reaction of sodium acid pyrophosphate and sodium bicarbonate. In most cases cornstarch is mixed with the acid pyrophosphate, and the two are sold together. Sufficient starch is used to make a product 2 parts of which will neutralize 1 part of soda. The soda in proper proportion may be added to the acid pyrophosphate and starch, however, and thus form a complete baking powder. This kind of baking powder is not sold, as a rule, to the household trade. It contains a somewhat larger quantity of carbon dioxide than household baking powder and is calculated to meet the needs of commercial baking conditions.

SODIUM ACID PYROPHOSPHATE BAKING POWDER

	Percent
Sodium bicarbonate	30. 59
Cornstarch	29. 03
Sodium acid pyrophosphate	40. 38
Total	100. 00

There is some question as to just what reaction products are formed with this baking powder. The following equation may represent the reaction:

$$Na_2H_2P_2O_7+2NaHCO_3=Na_4P_2O_7+2CO_2+2H_2O$$

All the foregoing formulas except the last are so proportioned as to give baking powders that will yield theoretically approximately 14 percent of total carbon dioxide. The fourth yields 17 percent. Fourteen percent is the strength ordinarily desired for the household trade, whereas that made for the commercial-baking trade usually contains from 16 to 17 percent of total carbon dioxide. Monocalcium phosphate and S. A. S. phosphate powders are also made especially for bakers' use.

In making a baking powder of a specified strength, the manufacturer takes a definite quantity of sodium bicarbonate and adds to this sufficient acid-reacting material to neutralize the soda present. Enough cornstarch is then added to make a product that has the desired gas strength. In other words, the cornstarch constitutes the difference, in percentage, between the sum of the percentages of the sodium bicarbonate and acid-reacting material and 100.

The cornstarch also separates and coats the particles of soda and acid-reacting materials, thereby increasing the stability of the baking powder in the can. The cornstarch is not an active ingredient of a baking powder, although it serves a useful purpose. The bicarbonate of soda and the acid-reacting materials are essential constituents.

The different types of baking powder react somewhat differently when mixed into a dough or batter. A tartrate baking powder will

react completely at room temperature, but owing to the high viscosity of a batch of dough, the gas will be largely retained for a considerable period of time. A straight phosphate powder will yield two-thirds of its gas at room temperature, but heat is required to liberate the remainder.

A combination powder will liberate one-fifth to one-third of the gas at room temperature, and the remaining gas after heat is applied. Those baking powders that require heat for the complete liberation of the gas are largely used in restaurants and commercial bakeries, where it is necessary to keep the batter or dough for long periods before baking.

Now nearly all baking powder manufacturers produce baking powders in which the speed of reaction is controlled to suit the requirements of the baker. In baking powders that contain S. A. S. as one of the ingredients, the manufacturer chooses an S. A. S. that has received such heat treatment in its manufacture that it will react at the speed desired. In like manner, an anhydrous monocalcium phosphate will not react in the cold nearly so rapidly as a hydrated acid phosphate. The presence of small quantities of other substances, such as calcium sulfate, calcium lactate, etc., also slows down the speed of reaction.

Total carbon dioxide is all the carbon dioxide present in a baking powder.

Residual carbon dioxide is the carbon dioxide retained in the baking-powder residue after treatment with water and heat.

Available carbon dioxide is the difference between the total and residual carbon dioxide and is the quantity of carbon dioxide liberated from a baking powder under leavening and baking conditions.

Analysis of Baking Powder

PREPARATION OF PRODUCT FOR ANALYSIS

In order to obtain a representative sample of baking powder for analysis the entire contents of the package should be removed and passed through a 20-mesh sieve and thoroughly mixed.

This procedure is necessary in order to assure a truly representative portion. If the baking powder has stood in a can for a considerable period of time, there is a possibility that more or less moisture has gained access to it and caused some reaction between the acid-reacting material and the soda. A sample containing an undue proportion of this reacted material could not be considered a representative sample; hence the necessity for thorough mixing.

Deterioration is generally manifested by the conversion of the powder into lumps or a solid cake.

METHODS OF ANALYSIS

Baking powders may be analyzed for all their constituents. The results of such analyses were published in 1924 in the annual foods and drugs report of the State of Alabama (*10, pp. 76–77*). These baking powders were analyzed for moisture, total carbon dioxide, available carbon dioxide, sodium oxide, calcium oxide, aluminum

oxide, potassium oxide, ammonia, phosphoric anhydride, tartaric anhydride, sulfur trioxide, and starch. Methods for making all these determinations may be found in Official and Tentative Methods of Analysis (*2, pp. 184–190*).

As a rule, however, the routine analysis of baking powders is limited to determining the available carbon dioxide, testing for the presence of heavy metals, and ascertaining the components of the baking powder.

The available carbon dioxide, which is evolved during the preparation of the dough or batter and the baking of the product, is ordinarily determined by subjecting the baking powder to conditions imitating those of actual use. In making this determination the usual practice is first to determine the total carbon dioxide, then the residual, and by difference obtain the available. An indirect method of making any determination is undesirable, however, if a direct one can be used. A direct method has been proposed (*4*) for this determination when using the gasometric method soon to be described. In this method the baking powder is decomposed with a solution of ammonium sulfate and heat is applied to remove the gas, which is collected and measured under standard conditions. If the volume of gas, the temperature, and the barometric pressure are known, its weight can be obtained from published tables, and from this weight the percentage of carbon dioxide is calculated.

Details of two methods for determining total, residual, and available carbon dioxide are given in Methods of Analysis (*2*). One is a gravimetric method and the other a gasometric method. In the gravimetric method Knorr's apparatus is used. In this method the baking powder is decomposed with dilute acid, heat is applied, and the apparatus is aspirated. The gas is dried and collected in a solution of potassium hydroxide or in soda lime, precautions being taken to exclude moisture and carbon dioxide from the air drawn through the apparatus. The increase in weight of the potash bulb or the soda lime tube is taken as the weight of carbon dioxide liberated from the sample of baking powder used.

The gasometric method was suggested by J. R. Chittick. In this the baking powder is decomposed in a flask which is directly connected to a gas-measuring tube. After the volume of the gas, the temperature, and barometric pressure have been noted, the weight of the carbon dioxide is determined by referring to a table which gives the weights of carbon dioxide at different temperatures and pressures for various volumes. This method has been modified by the specifying of 1.7 grams of baking powder as the charge (*3*).

Methods for determining impurities in baking powder are given in detail in the Methods of Analysis. A baking powder is a food accessory and should comply with established standards for limits of impurities.

Methods for making qualitative tests for tartaric acid and tartrates, calcium, and phosphoric acid are also given in the Methods of Analysis (*2*). A good qualitative test for an aluminum compound is as follows (*7*): From 1 to 2 grams of baking powder are dissolved in 5 cubic centimeters of normal hydrochloric acid, and to this 5 cubic centimeters of three times normal ammonium acetate and 5 cubic centimeters of one-tenth percent solution of "aluminon," the ammonium salt of aurintricarboxylic acid, are added. After being mixed to allow

the lake formation to take place, the solution is made alkaline with ammonium hydroxide containing ammonium carbonate. A bright red precipitate which persists in the alkaline solution indicates the presence of aluminum. This method has been modified so that it may be used to determine aluminum quantitatively (*17*, *18*).

The kind of starch present may be ascertained by the aid of the microscope. Cornstarch is ordinarily used in baking powders.

Baking powders slowly deteriorate on standing, more rapidly if the can is frequently opened, or if mositure gains access to the baking powder, thereby causing some reaction between the acid material and the bicarbonate. A baking powder should keep satisfactorily for at least a year if it is stored under proper conditions.

A recent patent has been issued (*6*) describing a method of improving the keeping quality of baking powder. This method is based on the principle of like charges of electricity repelling each other. In this method the acid-reacting substance is electrostatically treated to give it a charge of like sign as the bicarbonate of soda, i. e., both must have either positive or negative charges.

THE PRODUCTION OF BAKING CHEMICALS

Bicarbonate of Soda

Bicarbonate of soda is the alkaline ingredient of practically all baking powders. It is relatively cheap and is one of the purest chemicals manufactured. In the United States it is all made by the Solvay process.

The ammonia-soda or Solvay process utilizes ordinary salt in the form of brine. This is an advantage in countries like the United States where salt is found in deep-seated deposits and is extracted by means of the salt well. The strong brine solution is run into saturation tanks, where it comes in contact with ammonia gas. The ammoniacal brine is forced under pressure into the carbonating tower through a pipe near the middle of the tower. The carbon dioxide is forced into the lower end of the tower and allowed to bubble through many perforated diaphragms. The reaction may be expressed as follows:

$$NaCl + NH_3 + H_2O + CO_2 = NH_4Cl + NaHCO_3$$

The bicarbonate of soda, being insoluble in the ammonium-chloride solution, is precipitated, drawn off, filtered, washed with cold water, and dried.

Sodium bicarbonate may also be formed by passing a current of carbon dioxide and steam over soda ash at a temperature of 80° C. This reaction is represented by the following equation:

$$Na_2CO_3 + CO_2 + H_2O = 2\ NaHCO_3$$

Cream of Tartar

Cream of tartar is potassium bitartrate or potassium-hydrogen tartrate. Its only commercial source is grapes. Tartrates exist in the grape as potassium bitartrate, calcium tartrate, and in small quantities as free tartaric acid. Most tartrates are obtained commer-

cially as a byproduct of the wine industry, principally from a certain variety of sour wine. Small quantities are obtained from the grape-juice industry. When the grapes are crushed and pressed in the preparation of wine most of the tartrate salts, being soluble, are contained in the juice. When the grape juice is allowed to stand, crude crystals of tartrates, called argols, are formed. Fermentation accelerates this deposition but is not absolutely necessary.

As a rule, branches of the grapevine are floated in the fermenting vats. During the fermentation the argols are gradually deposited on the branches and sides of the vats. The crystals carry down with them much of the coloring matter in the juice.

From the argols cream of tartar is made by a process of purification. They are powdered, dissolved in boiling water, and filtered to remove dirt and other foreign matter. The coloring matter is removed with bone black or other decolorizing material. The clear liquid is run into shallow vats, and as it cools the cream of tartar is deposited in thick masses of crystals. These may be further purified by being redissolved in hot water and recrystallized until finally pure white crystals are produced. The crystals are ground, the cream of tartar being marketed as a powder.

A dark deposit called lees settles at the bottom of a barrel of new wine that has been allowed to stand a sufficient time. The lees contains a larger proportion of calcium tartrate than do the argols, and are used extensively for the production of tartaric acid.

Tartaric Acid

Tartaric acid is obtained from the calcium tartrate and cream of tartar in the lees and argols by treating them with sulfuric acid, which liberates the tartaric acid and precipitates the calcium as an insoluble sulfate. The following equation represents the reaction:

$$CaC_4H_4O_6 + H_2SO_4 = H_2C_4H_4O_6 + CaSO_4$$

The calcium sulfate is removed by filtration, and by concentrating the filtrate the tartaric acid is obtained in large glassy crystals. These crystals are purified by being redissolved and recrystallized.

Efforts have been made to produce tartaric acid and cream of tartar synthetically, and several patents for such processes have been taken out both in the United States and Europe, but commercial success in this field has not yet been attained.

A considerable proportion of the cream of tartar and tartaric acid used in this country is imported. The imports in 1937 of argols, crude tartar, and wine lees amounted to 23,820,000 pounds, of crude calcium tartrate 4,756,000 pounds, and of tartaric acid 327,000 pounds. The imports came principally from France, Italy, Algeria, and Tunisia. In 1938 the total imports of these materials amounted to 31,745,083 pounds valued at $2,471,892.

Domestic production figures for 1937 are not available, but according to the Census of Manufactures for 1935 there were produced in the United States in 1935, 6,887,121 pounds of tartaric acid valued at $1,609,027 and 3,855,022 pounds of cream of tartar valued at $641,971. These were produced chiefly in California and New York.

Tartaric acid exists in four forms, which may be classified in two groups: (1) Optically active forms, d-tartaric acid and l-tartaric acid, and (2) optically inactive forms, racemic acid and mesotartaric acid. Only d-tartaric acid is produced commercially; the other forms do not occur in nature except in traces. Synthetic methods of preparation have had as yet no commercial application.

Calcium Acid Phosphate

Calcium acid phosphate is a very widely used baking acid. It is the sole leavening acid of straight phosphate baking powder for household use and constitutes from 5 to 14 percent of the combination sodium aluminum sulfate-calcium acid phosphate powders. It is used almost exclusively as the leavening acid in self-rising flour and is also used in phosphated flours.

At first the process of making calcium acid phosphate consisted in treating bone ash with sulfuric acid, removing by filtration the sulfate of lime formed, evaporating the solution of monocalcium phosphate and phosphoric acid, purifying this solution, neutralizing the free phosphoric acid, and drying. Monocalcium phosphate produced by this process was used as a baking acid and later as an ingredient of baking powder.

Since the early part of the twentieth century natural phosphate rock has been the chief source of phosphate used for food purposes. Formerly the rock was treated with surfuric acid, in which process the tribasic phosphate was converted into free phosphoric acid. The crude phosphoric acid usually contained small quantities of impurities, which had to be completely removed before it could be used for food purposes. The purified phosphoric acid was made into monocalcium phosphate by reaction with calcium carbonate. It was then dried in vacuum, milled to a fine granulation, and bolted to a uniform size.

The wet process of producing phosphoric acid has to some extent been supplanted by the volatilization processes, in which phosphorus is volatilized, oxidized to phosphoric anhydride, and condensed in a small quantity of water, yielding a concentrated solution of phosphoric acid (H_3PO_4). For the commercial manufacture of phosphoric acid by volatilization there are two processes. In one an electric furnace is employed and in the other a fuel-fired furnace. Both processes consist in smelting a properly proportioned charge of phosphate rock, siliceous flux, and carbon. A small portion of the phosphorus so liberated is combined with iron, and removed as ferrophosphorus. The remainder passes out of the charge, with gases, as vapor, and is then oxidized by combustion with the air to phosphorus pentoxide, which is hydrated to phosphoric acid. This volatilized acid is practically pure and has high neutralizing value; however, after its formation it is subsequently treated to reduce the impurities present to a minimum.

To the highly purified phosphoric acid a calculated quantity of calcium carbonate or calcium hydrate is added, producing monocalcium phosphate which is practically pure. The reaction is represented by the following equations:

$$2H_3PO_4+CaCO_3=CaH_4(PO_4)_2.H_2O+CO_2$$

$$2H_3PO_4+Ca(OH)_2=CaH_4(PO_4)_2.H_2O+H_2O$$

When the lime and phosphoric acid have been properly mixed, they are set aside to allow them to completely react. After aging, the product is crushed to a medium size to insure more uniform drying. When dry, it is milled to the desired granulation, and packaged for shipment.

Monosodium Phosphate

The process of manufacturing monosodium phosphate is similar to that employed in producing monocalcium phosphate; that is, some compound of soda, such as sodium carbonate, is thoroughly mixed in proper proportion with phosphoric acid to form monosodium orthophosphate. The reaction is:

$$Na_2CO_3+2H_3PO_4=2NaH_2PO_4+CO_2+H_2O$$

The product may be dried directly, or it may be dissolved and recrystallized. Monosodium phosphate, however, is not entirely satisfactory for use in a baking powder, largely on account of its hygroscopic property.

Sodium Acid Pyrophosphate

Sodium acid pyrophosphate is manufactured by heating monosodium orthophosphate to a temperature well below 250° C. The following reaction takes place:

$$2NaH_2PO_4+\text{heat}=Na_2H_2P_2O_7+H_2O$$

By carefully controlling the heating, manufacturers are able to convert practically all the sodium orthophosphate into the acid pyrophosphate. If the temperature is allowed to rise too high, the pyrophosphate loses another molecule of water and becomes sodium metaphosphate, as represented by the equation:

$$Na_2H_2P_2O_7+\text{heat}=2NaPO_3+H_2O$$

Sodium metaphosphate has no acid properties and is of little commercial value. Recent tests have shown that most of the acid pyrophosphates are practically free from metaphosphate.

Sodium acid pyrophosphate has much better keeping qualities than the sodium acid salts of orthophosphoric acid. It is nonhygroscopic and less energetic in its action on sodium bicarbonate than are the sodium orthophosphates. It reacts but slowly in the cold dough and exerts most of its leavening power during the actual baking process.

Sodium acid pyrophosphate is used sometimes as a substitute for the more expensive cream of tartar for baking purposes. It is slow acting and an efficient baking acid for cakes, doughnuts, and pastry. Its rate of reaction is controlled for the most part by conditions of manufacture. It is principally used by commercial bakers.

Sodium Aluminum Sulfate

Sodium aluminum sulfate (calcined) may be represented by the formula $Na_2SO_4.Al_2(SO_4)_3$. It is prepared from bauxite, a natural hydrated oxide of aluminum. The bauxite is washed, dried, ground,

and treated with sulfuric acid in lead tanks, heated by live steam, and settled. The liquid thus obtained, which consists of a solution of aluminum sulfate, is mixed with niter cake (sodium bisulfate) and soda ash (sodium carbonate) in proper proportions, purified, and filtered. It is then evaporated to a sirupy liquid, which is poured into pans, where it solidifies in cakes of sodium aluminum sulfate (S. A. S.). These cakes are broken up and heated to about 500° C., which removes the water, leaving calcined S. A. S. This is ground and graded to make a uniform granulated product.

Sodium aluminum sulfate reacts with soda in the presence of water like an acid. This property is due to the hydrolysis of the aluminum sulfate part of the compound as shown by the following equation:

$$Al_2(SO_4)_3+6H_2O=2Al(OH)_3+3H_2SO_4$$

The acid thus liberated reacts with the soda in a baking powder.

Sodium aluminum sulfate was put on the market in 1892, and for several years was used as the only acid-reacting material in numerous brands of baking powder. Such baking powders deteriorated very slowly. They reacted only slightly in the cold and had plenty of reserve gas for the products when heat was applied. This type of baking powder, however, has been superseded almost completely by a composite type in which both sodium aluminum sulfate and calcium acid phosphate are used as the reacting components.

Cornstarch

Cornstarch may be considered a chemical, although it is usually thought of as a food or a sizing material. In a baking powder it exerts no chemical action; its purpose is to prevent reaction between the soda and acid-reacting material until moisture is applied. It is a constituent of practically all baking powders. Cornstarch is obtained from maize kernels, which are steeped until softened and then coarsely ground. The starch is removed by washing and settling. In most climates the humidity of the air is so great that baking powders would deteriorate rapidly if some such diluent were not used. In some baking powders a thin coating of starch drys on the acid materials, forming a protective coating that largely prevents reaction until a liquid is applied. For use in baking powder, starch is specially dried to improve its blending properties and to retard deterioration of the baking powder.

Ammonium Carbonate

Ammonium carbonate is used to a limited extent in certain kinds of baked products as, for instance, some types of cookies. Ammonium carbonate or bicarbonate has the advantage of decomposing into two gases and leaving no solid residue. The disadvantage is that if a slight excess of ammonia remains in the baked product the taste and odor are very disagreeable.

Ammonium carbonate and bicarbonate are prepared commercially by subliming a mixture of powdered calcium carbonate, ammonium sulfate or chloride, and a small quantity of powdered wood charcoal.

The resulting product is a mixture of ammonium carbonate and ammonium bicarbonate. The reactions may be expressed as follows:

$$(NH_4)_2SO_4+CaCO_3=(NH_4)_2CO_3+CaSO_4$$

and

$$(NH_4)_2SO_4+CaCO_3+H_2O=(NH_4)HCO_3+CaSO_4+NH_4OH$$

On standing, the ammonium carbonate loses the elements of water and forms ammonium carbamate, $(NH_4)_2CO_3-H_2O=NH_4NH_2CO_2$, so that the ammonium carbonate of commerce is a mixture of ammonium-acid carbonate and ammonium carbamate. When heat is applied it decomposes into ammonia, carbon dioxide, and water, as shown by the formula below:

$$(NH_4)HCO_3.NH_4NH_2CO_2+\text{heat}=3NH_3+2CO_2+H_2O$$

Ammonium carbonate is not used as a component of a baking powder, but rather as a substitute. It is self-contained—that is, when heat is applied the compound decomposes into gases which may serve as leavening agents. Its use always has been restricted to a few types of products.

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